

Novel Real-Time Nondestructive Technology for Chemical and Structural Health Management of Solid Rocket Propellants

Sami Daoud¹, Michal J. Villeburn², Kevin D. Bailey³, Gordon Kinloch⁴

^{1,2,3} Raytheon Missile Systems, Tucson, Arizona, 85734, United States of America

sami_daoud@raytheon.com

mjvilleburn@raytheon.com

kdbailey@raytheon.com

⁴United Kingdom Ministry of Defense, Bristol, BS34 8JH, United Kingdom

DESBVRAAMPIM2a@mod.uk

ABSTRACT

An innovative prognostics and chemical health management (CHM) technique was developed, for quantifying and characterizing health status of a CL-01 composite solid rocket propellant of tactical rocket motors. The technique is a cutting-edge real-time nondestructive technology approach which utilizes Near Infrared (NIR) spectra (M. Blanco, and I. Villarroya, 2002) emitted by microPHAZIRTM NIR miniature handheld platform, developed by Thermo Fisher Scientific. Benchtop high-performance liquid chromatography (HPLC) and ion chromatography (IC) were utilized as baseline reference techniques for correlation to microPHAZIRTM NIR measurements.

To build a quantitative calibration model, near infrared spectra were acquired for twenty freshly manufactured mixes of CL-01 propellant formulae, which were iterated using a D-Optimal full-factorial design of experiment (DOE). Four-hundred eighty measurements were recorded and analyzed using Partial Least Squares (PLS) regression analysis for model building and method development (Schreyer, 2012). NIR results were correlated to spectra, which were produced using HPLC and IC reference techniques and were determined to be in precise agreement. All recorded measurements that were performed using microPHAZIRTM handheld platform were successfully validated with HPLC and IC measurements. An algorithm was developed for microPHAZIRTM NIR thus qualifying the platform as a real-time nondestructive test (NDT)/nondestructive evaluation (NDE) tool for quantification of primary chemical constituents of CL-01 composite solid rocket propellant. Primary chemical constituents of CL-01

comprise a binder, oxidizer, plasticiser, and antioxidant/stabilizer.

Data sets for Shore-A hardness of each of the twenty DOE mixes were collected and used to calculate elastic modulus, tensile strength and percent strain. Calculated results conformed to specification requirements for CL-01 solid rocket propellant, henceforth confirming use of Shore A hardness as a real-time nondestructive test technique for validation of structural health of a solid rocket propellant.

This teaming effort between Raytheon Missile Systems (RMS), United Kingdom Ministry of Defence (UK MoD), Alliant Techsystems Launch systems (ATK LS), and Thermo Fisher Scientific demonstrated outstanding ability to utilize miniature cutting-edge technology to perform real-time NDT of CL-01 composite solid rocket propellant without generating chemical waste and residue and to ameliorate RMS technology base to capture incipient failures before the fact. The new technique will further be adapted for use to measure primary chemical constituents of other solid rocket propellants, liquid propellants, and composite explosives. The new technique will significantly reduce costs associated with surveillance and service life extension programs (SLEPs), which are often destructive and requires use of lengthy and expensive test techniques described in North Atlantic Treaty Organization (NATO) Standardization Agreement (STANAG)-4170 and Allied Ordnance Publication (AOP)-7 manuals.

1. INTRODUCTION

Tactical missiles are often exposed to severe thermal and dynamic stressors, often associated with long-term exposure to harsh environments, during transportation handling, transportation vibration, ejection and launch shock, diurnal cycling, storage, or when fielded. These stressors may act

Sami Daoud et al. This is an open-access article distributed under the terms of the Creative Commons Attribution 3.0 United States License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

individually or synergistically to factor into the aging, deterioration, and eventual decommissioning of critical warfighting assets. As a result, adverse impact and henceforth degradation reliability and/or safety of the assets may occur and will affect the total life cycle cost of fielding these weapon systems in a high state of readiness. Reliability analyses of legacy data indicated failure occurrences in missile structures, energetic and electronic components, all often associated with long-term exposure to static (heat, humidity, salt, etc.), and dynamic (transportation shocks, vibration, etc.) stressors.

Today's most common methods of NDT for evaluating the health of energetic systems are radiographic (X-ray imaging, X-ray computed tomography (CT), etc.), electrical (Eddy-current and electro-magnetic methods), dye penetrant, acoustic and ultrasonic, or a combination thereof. These methods are used by manufacturers during production processes, and mostly for quality control. Moreover, for fielded tactical missile systems, these methods are impractical for use. For health monitoring in the field, deployable portable platforms such as microPHAZIR™ NIR handheld platform become valuable as NDT/NDE tools.

A joint teaming effort was carried out between the UK Ministry of Defence (MoD), Raytheon Missile Systems, ATK Launch Systems, and Thermo Fisher Scientific to qualify microPHAZIR™ NIR platform as a miniature portable real-time NDE tool. The effort was successfully executed and would enable RMS, other defense contractors, US DoD and UK MoD to quantify primary chemical constituents of CL-01 solid rocket propellant nondestructively and on real-time basis. CL-01 is a composite high volumetric ballistic potential solid rocket propellant used in the propulsion subsystem of tactical missiles. Successful qualification of microPHAZIR™ NIR platform to quantify primary chemical constituents of CL-01 will enable defense contractors, DoD and MoD personnel to adapt this technology to quantify chemical constituents of all composite solid rocket propellants, liquid propellants, and warhead explosives, henceforth institute a cutting-edge technology of chemical health management (CHM).

Concurrently, RMS under the direction of UK MoD has successfully validated a new technique for determining structural health of CL-01 solid rocket propellant, also nondestructively and on real-time basis, henceforth integrating structural health management (SHM) with chemical health management (CHM). The combined techniques introduce a novel approach to prognostics and health management (PHM) of composite solid rocket propellants and warhead explosives.

The proposed technology is a proactive real-time NDE/NDT technique which replaces the old destructive test methodologies, described in NATO STANAG-4170 and AOP-7 manuals, imposed by Surveillance and Life

Extension Programs (SLEPs) of past and present day techniques. The proposed technology is a novel cutting-edge achievement as a NDT tool, in that it will define new means for quantifying chemical constituents of multi-component solid rocket propellant formulae while at the same time shedding light on propellants structural health, and will enable the manufacturer to define the anticipated residual useful life (RUL) of solid rocket propellants from a chemical as well as structural perspective. This achievement will shed valuable information about the anticipated mechanical and structural behavior of the solid rocket propellant matrix, in what is often referred to as "the chemical-mechanical link". The combination of chemical and mechanical (structural) health of the solid rocket propellant is the definition of prognostics and health management (PHM) and is the basic principle which will define whether a rocket motor (propulsion subsystem) would be warranted as "safe and suitable for service (S3)".

Today RMS and the UK MoD surveillance strategies seek to extend time between periodic surveillances, henceforth reducing tasks associated with subsystem breakdown, test and criticality analysis (BTCA) by as much as 50% or more. On average, a surveillance program is often recommended once every 3 to 4 years on a sample population which represents the fielded and/or stored weapons inventory. With the introduction of microPHAZIR™ NIR real-time technology and associated structural health management, it will be feasible to extend the time between surveillance programs activities and/or reduce the number of assets that have to undergo surveillance. When a SLEP plan is established for solid rocket motor (propulsion subsystem) subsystem, complex steps must be executed and comprise disassembly, dissection and extraction of propellant samples, followed by extensive testing (physical, chemical, hazards, and mechanical tests) of the rocket motor solid rocket propellant matrix, often referred to as "breakdown, test and criticality analysis (BTCA)". BTCA coupled with arena testing (static fire) of the solid rocket motor as well as other subsystems are challenging tasks, from manpower, cost and schedule perspectives, and therefore the need to exercise cost controls while at the same time maintain absolute confidence in assets health demand that novel technology approaches such as those associated with microPHAZIR™ NIR platform and more advanced (exploratory) technologies become integral part of SLEP. The ultimate goal is to be able to (i) predict subsystems, and henceforth system anomalies proactively and sufficiently in advance to institute corrective actions and/or preventive measures; (ii) ensure that the subsystem is reliable from a performance as well as safety perspective to fulfill warfighters requirements; and (iii) reduce generated chemical waste, logistics footprint, logistics response time, and life-cycle costs, which will ultimately increase systems availability, and enhance customer-supplier business relationship.

The ultimate goal of the proposed technology will be that of enabling RMS and the customer (UK MoD) to realize early warnings of unsafe conditions using real-time data, collected via microPHAZIR™ NIR miniature handheld platform and other advanced technologies of Thermo Fisher Scientific. Gaining real-time knowledge about the current health of a propellant or explosive matrix will offer effective insight to predicting residual useful life (RUL) of the system and its corresponding inventory.

Successful application of microPHAZIR™ NIR handheld platform as a NDE/NDT tool is the cornerstone and the spring board for future development of PHM of energetic subsystems: Cartridge Actuated Devices (CADs), Propellant-Actuated Devices (PADs), and electro-explosive devices (EEDs) of tactical and strategic missiles. MicroPHAZIR™ NIR handheld platform offers enormous potential for applications requiring real-time monitoring of the health status of warheads and solid rocket motors which have been exposed to fatigue resulting in chemical and mechanical (structural) degradation.

2. EXPERIMENTAL

A D-Optimal Design of Experiment (DOE) was initiated using Minitab 16, with the goal of manufacturing twenty laboratory scale mix iterations of CL-01 (L. Biegert, and B. Cragun, 2013) solid rocket propellant. The twenty mix iterations are listed in Table 1.

Table 1: DOE Design Series for Primary Constituents

Mix Number RBC1691-99-	Mix #	Oxidizer	Plasticizer	Antioxidant	Binder	TOTAL
38 (Bay 8)	1	84	3.25	0.350	12.400	100
39 (Bay 5)	2	84	3.00	0.275	12.725	100
40 (Bay 8)	3	82	2.75	0.300	14.950	100
41 (Bay 5)	4	85	2.50	0.300	12.200	100
42 (Bay 8)	5	83	2.50	0.325	14.175	100
43 (Bay 5)	6	85	3.25	0.275	11.475	100
44 (Bay 8)	7	83	3.00	0.300	13.700	100
45 (Bay 5)	8	81	3.50	0.350	15.150	100
46 (Bay 8)	9	82	3.00	0.350	14.650	100
47 (Bay 5)	10	82	3.50	0.275	14.225	100
48 (Bay 8)	11	83	2.75	0.350	13.900	100
49 (Bay 5)	12	83	3.50	0.250	13.250	100
50 (Bay 8)	13	85	3.00	0.250	11.750	100
51 (Bay 5)	14	81	2.50	0.275	16.225	100
52 (Bay 8)	15	85	2.75	0.325	11.925	100
53 (Bay 5)	16	81	2.75	0.250	16.000	100
54 (Bay 8)	17	81	3.25	0.325	15.425	100
55 (Bay 5)	18	84	2.50	0.250	13.250	100
56 (Bay 8)	19	82	3.25	0.250	14.500	100
57 (Bay 5)	20	84	3.50	0.300	12.200	100

For each mix, constituents were varied above and below specification limits (+1, -1), to capture acceptable high and low limits of each constituent within the formulation.

All CL-01 propellant raw materials were procured from ATK Allegany Ballistics Laboratory (ATK ABL) and were certified to material specifications. Raw materials which were utilized in the manufacture of the twenty DOE mixes are listed in Table 2. No hazards tests were required since all manufactured formulations were within the history of material sets prepared at ATK Launch Systems.

Table 2: CL-01 Propellant Raw Material Specifications

Material/Chemical	Specification
Prepolymer	MIL-H-85497
Oxidizer	MIL-A-82667
Curative	MIL-C-85498, Type II
Bonding Agent 1	HS 6-0823
Bonding Agent 2	MY 0510 HS 6-0093
Plasticizer	S273020C
Antioxidant	HS 6-0091
Combustion Stabilizer	MIL-Z-85500
Opacifier	HS 6-0090

Each of the twenty mix iterations amounted to 600 grams (1-pint each). Each of the twenty CL-01 propellant mixes was prepared using a 1-pint Baker Perkins mixer. At the conclusion of the mix cycle, each of the twenty 1-pint mixes was vacuum-cast into a Teflon-tape -lined carton. The Teflon tape facilitated carton removal and simulated a production-tooling surface. Each of the twenty mixes was cast to produce a rectangular- shaped block of 2.5-cm in width, 10-cm in length, and 12.5-cm in height, as depicted in Figure 1.

The front face (A) was arbitrarily identified as the surface that matched the label of the carton. The B surface is the top surface, the side from which the carton was cast.

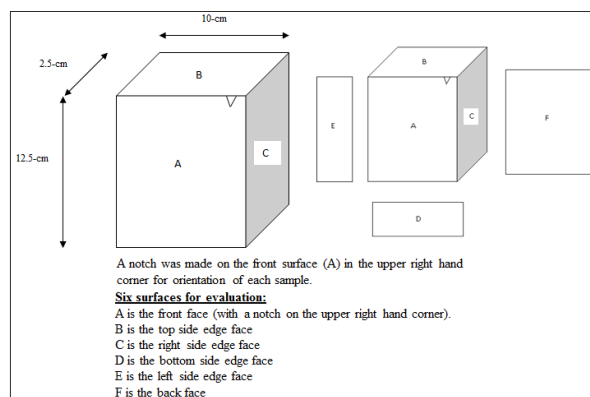


Figure 1: Sample Geometry and Sampling Locations

Upon vacuum-casting and cure of each of the twenty mixes, but prior to using microPHAZIR™ NIR platform for testing of mix constituency, Shore A hardness measurements were recorded instantaneously, at 10-second, and 15-second residence time. Table 3 summarizes shore A hardness measurements. Shore A hardness testing was performed on side B of all cast cartons. All propellant mixes experienced cure cycles of $145^{\circ}\text{F} \pm 5^{\circ}\text{F}$ for $192 \text{ hours} \pm 24 \text{ hours}$. A mix would be removed from the cure oven if and only if shore A hardness conformed to minimum required specification.

Table 3: Shore A Hardness of the Twenty DOE Vacuum-Cast Mixes

Mix Number RSC1691-09-	Sample #	Oxidizer	Plasticizer	Antioxidant	Binder	TOTAL	Shore A Ambient Temperature		
							Instant	10 Sec	15 Sec
38 (Bay 8)	1	84	3.25	0.350	12.400	100	71	56	54
39 (Bay 5)	2	84	3.00	0.275	12.725	100	72	59	58
40 (Bay 8)	3	82	2.75	0.300	14.950	100	71	57	56
41 (Bay 5)	4	85	2.50	0.300	12.200	100	79	74	73
42 (Bay 8)	5	83	2.50	0.325	14.175	100	75	63	61
43 (Bay 5)	6	85	3.25	0.275	11.475	100	65	50	48
44 (Bay 8)	7	83	3.00	0.300	13.700	100	66	51	49
45 (Bay 5)	8	81	3.50	0.350	15.150	100	45	35	33
46 (Bay 8)	9	82	3.00	0.350	14.650	100	70	57	55
47 (Bay 5)	10	82	3.50	0.275	14.225	100	68	51	49
48 (Bay 8)	11	83	2.75	0.350	13.900	100	73	58	57
49 (Bay 5)	12	83	3.50	0.250	13.250	100	63	50	48
50 (Bay 8)	13	85	3.00	0.250	11.750	100	70	54	52
51 (Bay 5)	14	81	2.50	0.275	16.225	100	70	56	55
52 (Bay 8)	15	85	2.75	0.325	11.925	100	67	57	56
53 (Bay 5)	16	81	2.75	0.250	16.000	100	69	58	56
54 (Bay 8)	17	81	3.25	0.325	15.425	100	67	54	52
55 (Bay 5)	18	84	2.50	0.250	13.250	100	66	59	58
56 (Bay 8)	19	82	3.25	0.250	14.500	100	65	54	53
57 (Bay 5)	20	84	3.50	0.300	12.200	100	63	54	53

2.1. Instrumentation

2.1.1. The microPHAZIR™ (NIR) Platform

Near Infra-Red (NIR) spectroscopy (H.W. Siesler, Y. Ozaki, S. Kawata, and M. Heise (Eds), 2002) is a well-established technique, which has been widely used since the mid-1970s. Only recently has new technology permitted NIR systems to be miniaturized into truly handheld system. One of the most important products is the microPHAZIR™ NIR handheld platform. MicroPHAZIR™ NIR handheld platform is based on near-infrared spectroscopy ((H.W. Siesler). The near-infrared region, depicted in Figure 2 is located between the infrared and visible region with wavelengths that range from 800-900 nanometers to 2500 nanometers.

MicroPHAZIR™ NIR handheld platform was developed by Thermo Scientific and is based on vibrational spectroscopy (*microPhazir™* User Manual). All molecules perpetually rotate, move, and contort in a complex manner at temperatures above absolute zero. Vibrational spectroscopy probes these contortions (or vibrations) of a sample to determine the chemical functional groups present. A common type of vibrational spectroscopy is infrared (IR) absorption/reflectance. It relies on illumination of the sample with optical radiation to probe the molecular vibrations.

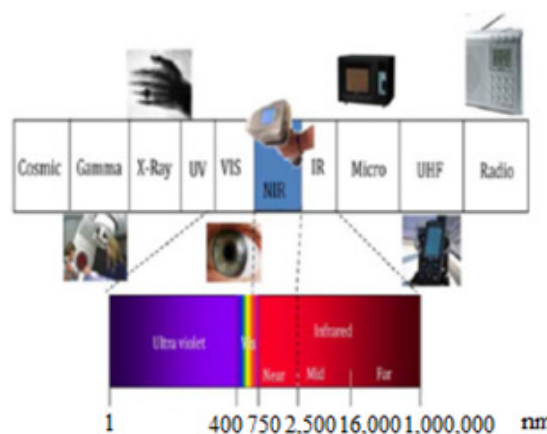


Figure 2: Near Infrared Region of the Light Spectrum

In NIR spectroscopy, the sample is illuminated with a broad spectrum of light in the near-infrared region and the transmission or reflection is recorded as a function of the frequency of the incident light. When the frequency of incident light equals the frequency of a specific molecular vibration, the sample tends to absorb some of the light. A material “fingerprint” results from recording the amount of light absorbed as a function of the wavelength (or frequency). The instrument is depicted in Figure 3. MicroPHAZIR™ NIR is a rugged handheld chemical identification unit designed for point-of-use applications, either in contact or analysis can be conducted through transparent bags and vials. This product allows the identification of chemicals and white powders using the principles of NIR spectroscopy. It is enclosed in a lightweight, rugged, resistant package. The microPHAZIR™ handheld contains a broadband NIR source, a Hadamard interferometer to separate the different wavelengths of light interacting with the sample, and a detector to collect the resulting energy.

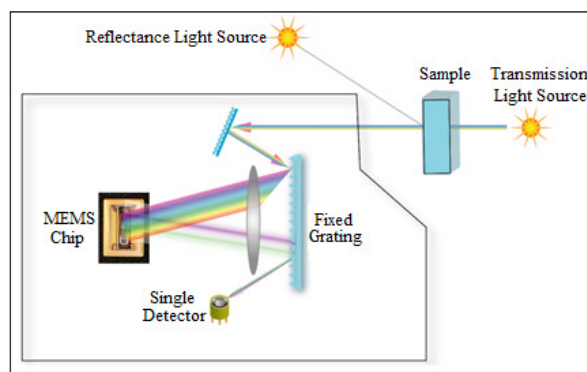


Figure 3: MicroPHAZIR™ NIR and Principle of Operation

2.1.2. Agilent 1100 HPLC Platform

Agilent 1100 Series system with different configurations comprises a vacuum degasser, isocratic pump, high-pressure binary pump, low-pressure quaternary pump, autosampler, thermostatted column compartment, variable wavelength detector and diode array detector. Key measurements are necessary to evaluate the performance of HPLC systems. Some characteristics are influenced by only one part of the system. For example, linearity, spectral resolution and detection limits are influenced mainly by the detector, delay volume and composition accuracy by the pump and carryover by the autosampler. In contrast, other characteristics such as baseline noise and precision of retention times and peak areas are influenced by the complete system. This note describes the following measurements:

- I. Detector — baseline noise, drift, wander, linearity, spectral resolution, sensitivity.
- II. Pump — composition accuracy, precision, ripple, precision of retention times, delay volume.
- III. Column compartment — temperature stability.
- IV. Autosampler — precision of peak areas, linearity, carry-over.

2.2. Chemical Health Management (CHM)

2.2.1. NIR Measurements/Data Collection

The primary measured constituents of CL-01 solid rocket propellant are listed herein:

- I. Agerite White anti-oxidant/stabilizer.
- II. Ammonium perchlorate (AP) Oxidizer.
- III. Dioctyl Sebecate (DOS) plasticizer.
- IV. Hydroxyl-terminated polybutadiene (HTPB) binder, and is determined by difference between the sum of the primary constituents in (I), (II), and (III) and 100%.

Measurements were performed on two platforms: microPHAZIR™ NIR handheld platform and Agilent 1100 High-Performance Liquid Chromatograph (HPLC) platform. In the case of microPHAZIR™ NIR handheld platform, measurements were performed and recorded on each of the six faces of each of the twenty rectangular blocks, as depicted in Figure 4.

Upon manufacture and vacuum casting of each propellant mix and prior to performing measurements, 3-mm of the binder-rich surface of each cast block is peeled-off and removed from the surface, exposing the homogeneous material.

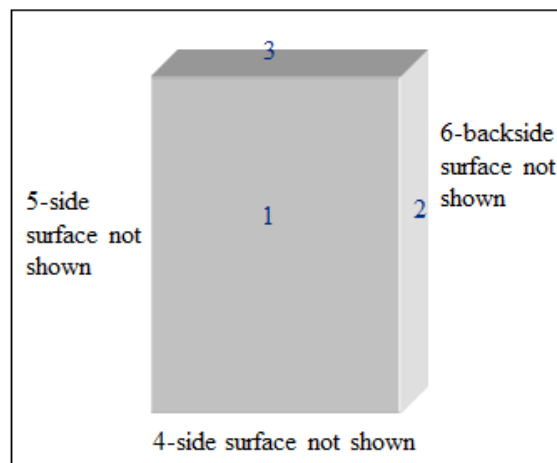


Figure 4: Vacuum-Cast Propellant Blocks, Depicting six Measured Surfaces

All 20 sample blocks were measured at ATK Launch Systems on June 26, 2013. The instrument used was microPHAZIR-GP Probe (part number 800-00259-01) with microPHAZIR Fiber Optic Probe Accessory (part number 810-01351-01). The instrument serial number was 2575 shown in Figure 3. The optical fiber probe attachment is depicted in Figure 5. The overall platform assembly is depicted in Figure 6 and Figure 7. Prior to taking measurements, microPHAZIR™ NIR platform was turned on and allowed to warm up for five minutes. A self-test pass was verified to ensure the unit was working properly.



Figure 5: Optical Fiber Probe

Samples were measured in sample number order starting with sample 1 (ATK mix number RBC1691-99-38) and ending with sample 20 (ATK mix number RBC1691-99-57). Each sample was measured in quadruplet and consecutively on each of its six faces/sides. The four measurements per face/side were collected at different positions. For each measurement, the tip of the optical fiber probe was placed in contact with the sample and perpendicular to the sample face so that the probe tip was flat against the sample surface. The instrument trigger was then activated to initiate an approximately three-second scan. Prior to collecting the four measurements per face, a

background measurement was taken of the built-in reflectance standard. The measurement technique is shown in Figure 6 and Figure 7.

Sample-averaging was performed in MATLAB. All other analyses were performed in Thermo Method Generator (TMG), version 4.0.1.0 (*microPhazir*TM User Manual).



Figure 6: Sample Side Measurement Technique



Figure 7: Sample Top Measurement Technique

2.2.2. Model Building (Schreyer, 2012)

2.2.2.1 Data Collection

CL-01 Spectral data using *microPHAZIR*TM NIR handheld platform followed best practices outlined by the platform manufacturer, as follows:

- I. Obtain representative samples for the library.
 - A. Obtain realistic sample mixes that will form the library. These sample mixes should be representative of the CL-01 material that will be identified. No selectivity is implied for materials until the library is built and validated.

- B. Measure samples, as illustrated in Figures 6 and 7. Perform measurements in triplicate.

- C. Label all materials with name (Group ID or Method/Sample), and if appropriate reference value for PLS quantitative analysis.

- D. Transfer all names into a “.csv” file, and then use this to populate “GroupID.csv” on the *microPHAZIR*TM “Config” directory.

II. Obtain reference values.

- A. For quantitative analysis, the full range of measurement shall be included in the library. Models only are considered robust over the data range actually referenced.

- B. Obtain replicate samples for at least 3 points over the measurement range.

- C. For realistic model building (Schreyer, 2012), at least 10 reference values over the measurement range shall be obtained. As the size of the range increases, so should the reference values collected. Since samples may change over time, it is appropriate to collect the spectra from the same sample as the reference values are obtained from.

2.2.2.2 Spectral Generation

I. Pre-spectral collection

- A. Prior to collecting spectra ensure that self-test performance qualification (PQ) has been performed.

- B. Ensure that group identifications (group ids) are transferred into GroupID.csv.

- C. Also ensure that the Group ID name is the correct name for the material and is present on the Collect screen on the *microPHAZIR*TM.

II. Spectral collection

- A. The minimum number of spectra collected for any library building is triplicate scans in 3 positions. Position the nose of *microPHAZIR*TM firmly against the material to be measured, as depicted in Figure 6 and Figure 7 (left), and take triplicate scans of the material without moving the sample. This will give information about instrument variability. Repeat twice.

- B. Repeat measurements for each side of the block.

- C. Repeat steps (A) and (B) for each mix.

2.2.2.3 Spectral Evaluation

I. Initial spectral evaluation.

- A. Load the collected data into Method Generator

- B. Ensure that there are no data which show absorbance (y-axis) past 3.

C. Observe if there are any noisy spectra, especially at high absorbance. If so, delete them. These usually arise if the trigger was pressed either without a sample in front or if sample is inadequate.

D. Highlight each group to make sure that all spectra look similar in the same group. Any obvious single outliers may be deleted. The best scenario is when the triplicate scans are right on top of each other, and there is little difference between positional scans. However, as long as the positional replicates appear similar and are close together, this is adequate. If one position is obviously off from the others, keep it, but watch to see if it affects the final results.

E. Delete any spectra where there was awareness of probable mistake in measurement. Do not delete scans just to make everything pretty. Deviations from the norm could be due to actual inherent sample differences and will need to become part of the model.

F. Reference values must be inputted at this time, using the Edit Y-value option.

G. Save the final edited data.

II. Method generation

A. Progress through the standard preprocessing options, and then evaluate the model using Spectral Match.

B. Adequate separation should be observed between samples. There should be a gap between the colors associated with one group and the next closest color of the nearest group.

C. Save the model if the model is acceptable.

D. Load the data files onto the microPHAZIR™ to test the model.

III. Method validation

A. Load a set of spectra into method generator (MG). For true method validation these should be unique spectra, not used in library building.

B. Select Model I Model validation. Browse to locate the application. Press OK

C. A panel will open with the validation results. It will be sorted by sample groups. Therefore it is very important that the GroupID of new spectra be identical to the GroupID of the library spectra. Otherwise a No ID label will be inserted.

D. The results show number of mismatches, false positives/false negatives, and then the full results of the model validation for each material. It will list the top 3 matches returned and their associated correlation coefficients.

E. The results can be saved as a “.csv” file by selecting File | Save all

2.3. Benchtop HPLC/IC Measurements/Data Collection

Prior to conducting measurements, approximately 3-mm of the surface of each of the 20 cast samples was removed. This process is often performed on freshly manufactured mixes because the first 3-mm of a cast composite propellant is often binder-rich. To maintain consistency in measurements, the binder-rich region was removed with a special cutting tool.

Following microPHAZIR™ platform measurements, 0.5- to 1-gram weight samples were removed from the measured regions and analyzed using HPLC and IC to determine the following (Mattos et al., 2004):

- a. AP oxidizer content.
- b. Agerite White stabilizer/antioxidant content.
- c. DOS plasticizer content.
- d. HTPB binder content (by difference).

HPLC and IC analyses of samples removed from the six surfaces of each of the twenty mixes are summarized in the results in section 3. For HPLC, samples were extracted overnight at a level of 50 mg/mL in stabilized tetrahydrofuran. Samples were prepared in triplicate. Sample extracts were analyzed using an HP1090 HPLC equipped with a C8 column and a diode-array detector. Approximately 200 milligrams were used for each sample preparation. A sample portion was cut with a razor blade into several pieces to facilitate extraction.

The antioxidant was identified by HPLC analysis (Urbanski et al, 1977) using a standard for identification. The antioxidant is often associated with the pre-polymer/binder matrix. The plasticizer was also measured using HPLC analysis (Urbanski et al, 1977).

IC samples were prepared by extracting 100 mg of propellant in 200 mg of deionized water. To facilitate the complete extraction of the AP from the propellant matrix, the propellant was leached for at least seven days in the water under ambient conditions. This may be a conservative amount of leach time, but evaluation after a 48-hour leach was shown to be inadequate. Exact weights of both the propellant sample and deionized water were recorded to at least four significant figures and used in the calculation. The chromatographic conditions of the analysis were performed as follows:

- Instrument: Dionex 500 IC System 4 with anion suppressed/conductivity detector
- Column: IonPac® AG4 guard column (4X50 mm)
- Eluent: 40 mM NaOH
- Flow rate: 1.2 ml/min
- Run time: 1.0 minute
- Elution time: 0.6 minutes
- Injection volume.: 10µLSRS Setting: 100 mA

- Calibration: bracketed
- Standards: 400.0, 430.0 and 460.0 ppm AP

2.4. Structural Health Management/Data Collection

Shore A hardness testing was performed on side B of all cast blocks, as depicted in Figure 1. Shore A hardness measurements were recorded at three residence times: instantaneous, 10-second, and 15-second residence times.

Measured values for shore A hardness were used to calculate elastic modulus, tensile strength, and percent strain for each propellant mix. Values were correlated to the specifications for CL-01. The primary goal of this technique is to validate mechanical integrity of the propellant real-time and nondestructively using shore A hardness measurement techniques. The approach would be utilized in conjunction with microPHAZIR™ handheld platform to determine structural as well as chemical health of CL-01 propellant and other composite propellants and explosives.

The following semi empirical formulae were used in calculating tensile stress, elastic modulus, and percent strain, respectively.

For Tensile Stress (TS), using 15-second Shore A hardness measurements, stress was calculated in equation 1 (Shore (Durometer) Hardness) as follows:

$$TS = 0.0423 (S_A)^{1.2799} \quad (1)$$

Where TS is tensile stress, in MPa, and S_A is Shore A hardness.

For Elastic Modulus E, using 15-second Shore A hardness measurements, E was calculated in equation 2 (A.N. Gent, 1958) as follows:

$$E = 0.0981 (56 + 7.66S)/0.137505 (254 - 2.54 S_A) \quad (2)$$

Where E is elastic modulus in MPa.

Percent strain was calculated, in accordance with Hook's law, as the ratio of stress, in equation (1) to elastic modulus, in equation (2).

3. RESULTS

3.1. NIR Spectra

Figure 8 depicts unprocessed (unfiltered) spectra for each of the twenty CL-01 propellant samples. Data sets were collected using microPHAZIR™ NIR handheld platform. Almost all spectra were visually the same; with very few outliers, which is a normal trend. For example, the spectra in light blue have obvious spectral artifact at the high end at the wavelength end.

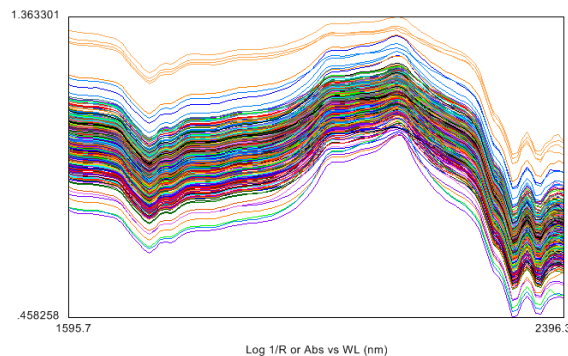


Figure 8: Unfiltered NIR Spectra (Absorbance vs. Wavelength)

These gross outlier spectra were removed (filtered) from the data sets (depicted in Figure 9). A total of 8 out of 480 (1.7 percent) spectra were removed as outliers leaving 472 spectra for use in the calibration and algorithm development models.

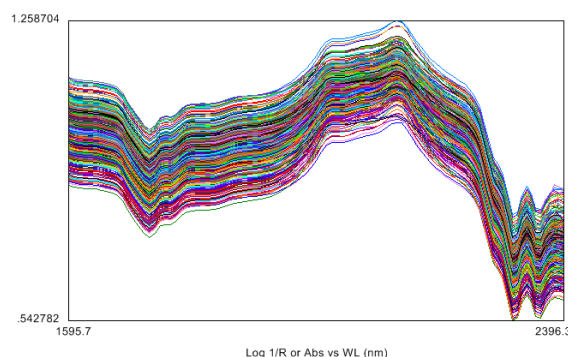


Figure 9: Filtered NIR Spectra (Absorbance vs. Wavelength)

For comparison, CL-01 propellant spectra and PBX(AF)-108 (S. Daoud, M. J. Villeburn, K. D. Bailey, G. Kinloch, L. Biegert, and C. Gardner, 2013) NIR spectra were plotted in Figure 10. It is observed that on average CL-01 spectra have approximately an absorbance near 1 and PBX have an absorbance near 0.4 (C. Gardner, and S. Schreyer 2013). This absorbance difference of 0.6 is translated to a $10^{-0.6}$, a factor of 0.25 of less light returned from CL-01 samples. This factor of four of less light is due to the gray color of CL-01 sample due to the presence of the opacifier in the formula. In general, the less light returned to the detector (due to higher light absorbance by the sample), the noisier the spectra.

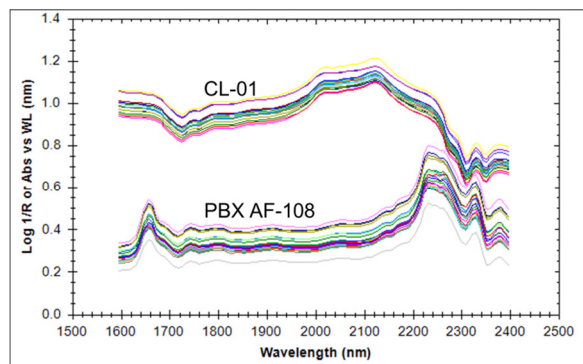


Figure 10: Comparison of Spectral Readings of CL-01 Propellant vs. PBX(AF)-108 Explosive

3.2. Spectral Preprocessing

To remove nuisance/noise variations from the NIR spectra before generating the calibrations models for algorithm development, the sample-averaged spectra were first filtered using Savitsky-Golay 9-point, 2nd-order, 2nd-derivative filtering technique. They were then range normalized so that each spectrum has zero mean and unity standard deviation.

Analysis was performed over the spectral range 1595–2250 nm, and this is the spectral range used for calibrations. Plots of the preprocessed spectra for each primary constituent are depicted in Figure 11.

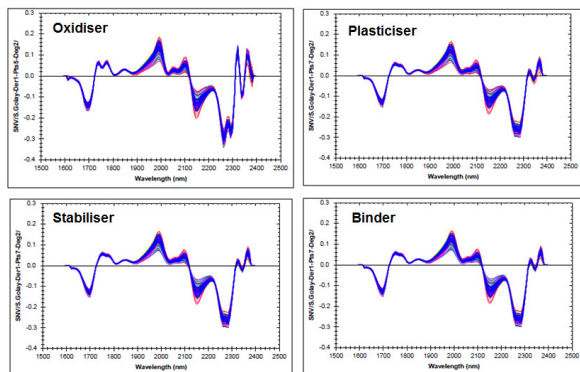


Figure 11: Sample Averaged, Pre-processed Spectra for the Four Primary Constituents of CL-01 Propellant

3.3. Design Points vs. microPHAZIR™ NIR Readings

Test sets collected with microPHAZIR™ NIR handheld platform for all twenty samples were analyzed using Thermo Method Generator (TMG) partial least square (PLS) analysis software and are listed in Table 4. Upon reduction and analysis of the data, findings indicated near identical readings between those measured using microPHAZIR™ NIR and those measured using benchtop HPLC/IC instruments.

Table 4: microPHAZIR™ NIR Measurements of Primary Constituents

Mix Number RBC1691-99-	Sample #	% Oxidizer	% Plasticizer	% Stabilizer	% Binder
38	1	83.71	3.15	0.29	12.38
39	2	83.88	2.83	0.23	13.11
40	3	81.89	2.69	0.29	15.27
41	4	84.85	2.45	0.18	12.48
42	5	83.39	2.68	0.28	13.99
43	6	85.29	3.05	0.13	11.57
44	7	82.05	2.64	0.24	14.90
45	8	80.81	3.36	0.25	15.67
46	9	82.25	2.59	0.28	14.40
47	10	82.94	2.98	0.21	13.79
48	11	83.12	2.58	0.24	14.02
49	12	83.18	3.15	0.17	13.61
50	13	85.06	2.97	0.17	12.30
51	14	80.83	2.60	0.21	16.80
52	15	83.76	3.05	0.24	13.19
53	16	80.13	2.75	0.20	17.01
54	17	80.44	2.95	0.23	16.34
55	18	82.70	2.66	0.15	14.68
56	19	81.35	2.96	0.21	15.32
57	20	82.70	3.58	0.16	13.35

The plotted spectra of Figure 12 through Figure 15 for the oxidizer, plasticizer, stabilizer, and binder respectively are the sample-averaged results of the measured readings using microPHAZIR™ NIR (plotted on the Y-axis) versus design values, plotted on the X-axis, which were those of the individual DOE design sets listed in Table 1.

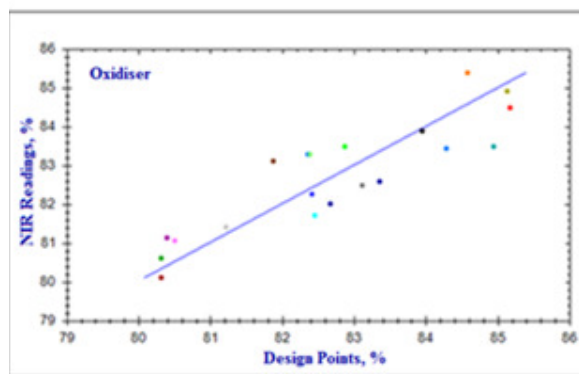


Figure 12: NIR Readings vs. DOE Design Points for the Oxidiser

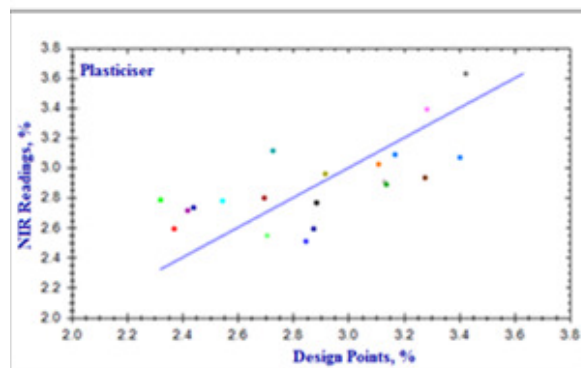


Figure 13: NIR Readings vs. DOE Design Points for the Plasticiser

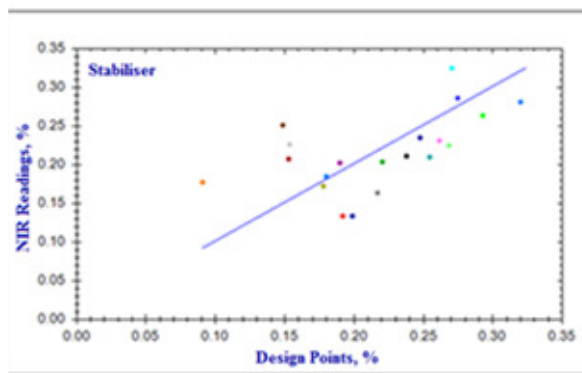


Figure 14: NIR Readings vs. DOE Design Points for the Stabiliser

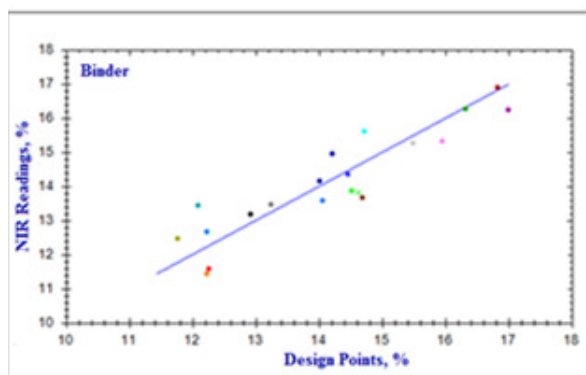


Figure 15: NIR Readings vs. DOE Design Points for the Binder

3.4. DOE Benchtop Analyses

Table 5 summarizes compositional results for each of the primary constituents in each of the 20 DOE sample mixes.

As illustrated in Figures 12 through 15 and Table 6, NIR values compare precisely well and within the allowable margin of error, to those measured using benchtop HPLC/IC and to DOE design sets of Table 1.

Table 5: HPLC Measurements of Primary Constituents

Mix Number RBC1691-99-	DOE Sample #	% Oxidizer	% Plasticizer	% Stabilizer	% Binder
38	1	84.29	3.17	0.32	12.22
39	2	83.95	2.89	0.24	12.92
40	3	82.46	2.55	0.27	14.72
41	4	85.17	2.37	0.19	12.26
42	5	82.87	2.32	0.29	14.51
43	6	84.58	3.11	0.09	12.22
44	7	82.67	2.88	0.25	14.21
45	8	80.51	3.29	0.26	15.94
46	9	82.42	2.85	0.27	14.46
47	10	81.88	3.28	0.15	14.69
48	11	82.39	2.71	0.27	14.63
49	12	82.36	3.40	0.18	14.06
50	13	85.13	2.92	0.18	11.77
51	14	80.40	2.42	0.19	16.99
52	15	84.94	2.73	0.25	12.08
53	16	80.32	2.70	0.15	16.83
54	17	80.32	3.14	0.22	16.32
55	18	83.35	2.44	0.20	14.01
56	19	81.22	3.13	0.15	15.49
57	20	83.12	3.42	0.22	13.24

Table 6: Comparison of Benchtop vs. Handheld Measurements of Primary Constituents

Mix Number RBC1691-99-	Sample #	% Oxidizer		% Plasticizer		% Stabilizer		% Binder	
		HPLC	NIR	HPLC	NIR	HPLC	NIR	HPLC	NIR
38	1	84.29	83.71	3.17	3.15	0.32	0.29	12.22	12.38
39	2	83.95	83.88	2.89	2.83	0.24	0.23	12.92	13.11
40	3	82.46	81.89	2.55	2.69	0.27	0.29	14.72	15.27
41	4	85.17	84.85	2.37	2.45	0.19	0.18	12.26	12.48
42	5	82.87	83.39	2.32	2.68	0.29	0.28	14.51	13.99
43	6	84.58	85.29	3.11	3.05	0.09	0.13	12.22	11.57
44	7	82.67	82.05	2.88	2.64	0.25	0.24	14.21	14.90
45	8	80.51	80.81	3.29	3.36	0.26	0.25	15.94	15.67
46	9	82.42	82.25	2.85	2.59	0.27	0.28	14.46	14.40
47	10	81.88	82.94	3.28	2.98	0.15	0.21	14.69	13.79
48	11	82.39	83.12	2.71	2.58	0.27	0.24	14.63	14.02
49	12	82.36	83.18	3.40	3.15	0.18	0.17	14.06	13.61
50	13	85.13	85.06	2.92	2.97	0.18	0.17	11.77	12.30
51	14	80.40	80.83	2.42	2.60	0.19	0.21	16.99	16.80
52	15	84.94	83.78	2.73	3.05	0.25	0.24	12.08	13.19
53	16	80.32	80.13	2.70	2.75	0.15	0.20	16.83	17.01
54	17	80.32	80.44	3.14	2.95	0.22	0.23	16.32	16.34
55	18	83.35	82.70	2.44	2.66	0.20	0.15	14.01	14.08
56	19	81.22	81.35	3.13	2.96	0.15	0.21	15.49	15.32
57	20	83.12	82.70	3.42	3.58	0.22	0.16	13.24	13.35

Plots of primary constituents of CL-01 which were measured using microPHAZIR™ NIR, and HPLC/IC are depicted in Figures 16 through 19 and are correlated to actual DOE design sets. In the figures, only the stabilizer shows noticeable deviation from the design sets, primarily because the sum of Agerite white oxidation products and AO2246 antioxidant, often associated with Agerite white, were both excluded from PLS analysis. Those two components have no effect on stability of the propellant and are quantitatively negligible (amounting to approximately 5%) in comparison to the total plasticizer content.

As a result, this effort confirmed the ability to use the microPHAZIR™ NIR miniature handheld platform as a non-destructive means for determining primary chemical constituents of solid rocket propellants, and was validated via benchtop measurements of HPLC and IC instrumentation.

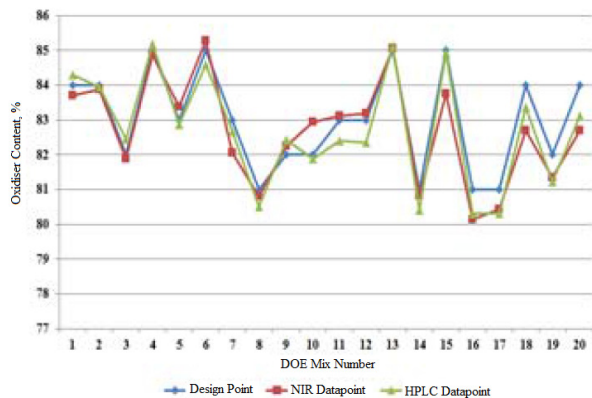


Figure 16: Comparison of NIR VS. HPLC Measurements to Actual Design Sets for Oxidiser Content

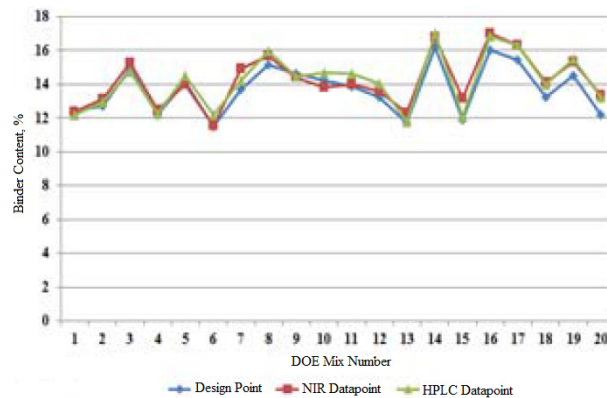


Figure 19: Comparison of NIR VS. HPLC Measurements to Actual Design Sets for Binder Content

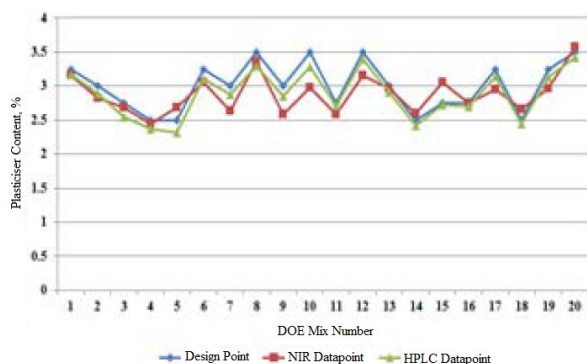


Figure 17: Comparison of NIR VS. HPLC Measurements to Actual Design Sets for Plasticiser Content

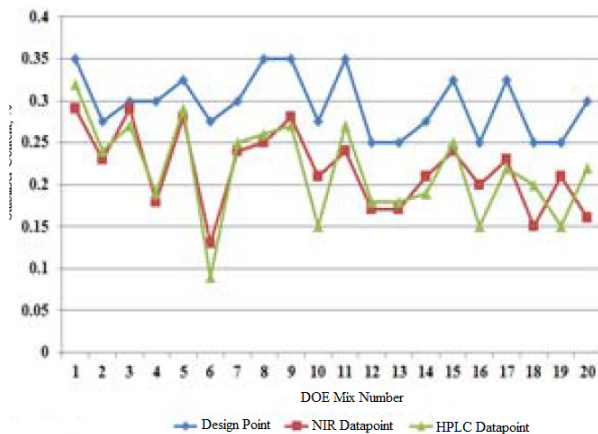


Figure 18: Comparison of NIR VS. HPLC Measurements to Actual Design Sets for Stabiliser Content

3.5. Structural Health Management

Three critical elements define prognostics and health management as a real-time nondestructive test technique. The first element is electrical health management (EHM), and primarily comprises built-in test (BIT). This field is mature and has been used for over five decades. The second element is chemical health management (CHM), as a real-time nondestructive test technique. This field has been under development for the past decade and is only gaining grounds with the recent work of RMS. This work is described in this white paper and in an earlier white paper published at the International Journal of Prognostics and Health Management, in October of 2013. The third element is structural health management (SHM). Structural health management is a real-time nondestructive test technique comprising two sub-elements. The first is real-time nondestructive radiographic x-ray technique, which sheds light on incipient structural failures associated with cracks and crack propagation or delaminations at the propellant-liner-interface (PLI). This element is also mature and has existed for many decades, henceforth is not a topic of discussion in this white paper. However it is an integral sub-element of RMS structural health management. The second and most important sub-element of structural health management is the collection of shore A hardness data followed by manipulation of the data to yield results on propellant elastic modulus (E), tensile stress, and strain. This technique is nondestructive and is an integral sub-element of structural health management, which is an integral element of PHM. Upon collection of shore-A hardness data, elastic modulus is derived using equation (2), defined as Gent semi empirical formula. Shore-A hardness results are also used, as described in equation (1) to calculate tensile stress (TS). Strain is then calculated using the general equation described below:

$$\text{Modulus (E)} = \text{Stress/Strain} \quad (3)$$

Table 7 lists instantaneous, 10-second and 15-second shore-hardness for each of the twenty cast sample mixes of the DOE design sets. The table also lists the calculated moduli for each mix and compares them to maximum and minimum specification. It is important to keep in mind that elastic modulus is calculated from the 15-second shore-A hardness data. Fifteen-second shore-A hardness data are most reliable because the Durometer indenter is allowed sufficient time to penetrate the polymer-based composite material and henceforth provides more accurate and realistic values about the physical nature of the material elasticity.

In Table 7, only sample mix 4 had a modulus value that exceeded maximum specification of 750 psi. This is an expected result considering that mix 4 comprised the highest amount of oxidizer and lowest amount of plasticizer.

Table 7: Calculated Mechanical Data for CL-01 Propellant Using Shore Hardness Measurements

ATK CL-01 Mix Number	DOE Sample #	Shore A Hardness			Calculated Values from Shore A Hardness			Specifications		
		10s	10-S	15s	Modulus, Psi	Tensile Strength, Psi	Stress, %	Modulus, Psi (Min-Max)	Stress, % (Min)	Tensile Strength, Psi (Min)
35 (Day 0)	1	71	56	54	415.9	1011.9	240.3			
36 (Day 0)	2	72	59	58	403.9	1038.9	238.1			
40 (Day 0)	3	71	57	56	440.1	1095.1	239.1			
41 (Day 0)	4	79	74	73	626.2	1408.2	186.3			
42 (Day 0)	5	73	63	61	346.9	1132.7	216.3			
43 (Day 0)	6	65	55	48	331.9	970.9	245.2			
44 (Day 0)	7	66	51	49	344.0	935.0	239.3			
45 (Day 0)	8	45	35	33	187.6	136.7	239.9			
46 (Day 0)	9	70	57	55	401.9	1030.9	239.9			
47 (Day 0)	10	66	51	49	344.0	935.0	239.3			
48 (Day 0)	11	73	58	57	405.0	1094.4	232.3			
49 (Day 0)	12	69	50	48	331.9	970.9	245.2			
50 (Day 0)	13	70	54	52	339.0	996.1	239.2			
51 (Day 0)	14	70	56	55	401.9	1030.9	239.9			
52 (Day 0)	15	67	57	56	440.1	1095.1	239.1			
53 (Day 0)	16	69	58	56	440.1	1095.1	239.1			
54 (Day 0)	17	67	54	52	339.0	996.1	239.2			
55 (Day 0)	18	66	59	58	401.9	1030.9	239.9			
56 (Day 0)	19	65	54	53	401.9	987.9	240.9			
57 (Day 0)	20	65	54	53	400.9	1207.9	273.8			

Validation of this structural test technique is ongoing, and recent results collected from actual baseline (time $t = 0$) solid rocket propellant, as well as the same propellant under accelerated-aged conditions (time $t = 1, 3$, and 6 month) have indicated excellent correlation between specifications for modulus, stress, and strain and data which were calculated from measured shore-A hardness. The technique of using Shore A and Shore D hardness will be adopted as an integral means of real-time nondestructive test technique in combination with x-ray radiography, for structural health management (SHM). This technique in combination with microPHAZIR™ NIR will be an integral part of prognostics and health management (PHM), as a real-time NDT/NDE test technique to future surveillance of solid rocket propellants and warhead explosives.

4. CONCLUSION

Datasets from both microPHAZIR™ NIR handheld platform and Agilent 1100 (Performance Characteristics) high-performance liquid chromatography (HPLC)/ion

chromatography (IC) platforms were precisely similar and representative of the constituents of CL-01 solid rocket propellant. In the case of microPHAZIR™ NIR handheld platform, dataset indicated excellent consistency and stability across the full datasets while at the same time closely representative of the results collected using Agilent 1100 high-performance liquid chromatography (HPLC)/ion chromatography (IC) platform.

The D-optimal full-factorial design of experiment (DOE) was successful in generating an algorithm for use in microPHAZIR™ NIR handheld platform for use in real-time quantitative determination of primary chemical constituents of CL-01 solid rocket propellant. Therefore, use of microPHAZIR™ NIR handheld platform for real-time non-destructive chemical quantification solid rocket propellants is a valid chemical health management (CHM) test technique, which alleviates the drawbacks of chemical waste and solid residue generation.

Of notable importance in this work is the concurrent success of using Shore-A hardness as a real-time nondestructive test technique for determining mechanical properties of the propellant, henceforth structurally monitors health of the propellant matrix (SHM).

Therefore, the combination of chemical and structural health management of the solid rocket propellant was successfully demonstrated in this work as a primary means of real-time prognostics and health management (PHM) technique for energetic and inert composite polymer based materials.

NOMENCLATURE

AF	Air Force
AOP	Allied Ordnance Publication
AP	Ammonium Perchlorate
ATK	Alliant Techsystems
BTCA	Breakdown, Test and Criticality Analysis
CAD	Cartridge-Actuated Device
CHM	Chemical Health Management
CT	Computed Tomography
DOS	Dioctyl Sebecate
DoD	Department of Defence
DSTO	Defence Science and Technology Organization
EED	Electro-Explosive Device
HPLC	High-Performance Liquid Chromatography
IC	Ion Chromatography
LS	Launch Systems
MoD	Ministry of Defence

NATO North Atlantic Treaty Organization
 NDE Non-Destructive Evaluation
 NDT Non-Destructive Testing
 NIR Near-Infrared
 PAD Propellant-Actuated Device
 PBX Plastic-Bonded Explosive
 PHM Prognostics and Health Management
 PLS Partial Least Square
 SHM Structural Health Management

REFERENCES

- S. Daoud, M. J. Villeburn, K. D. Bailey, G. Kinloch, L. Biegert, and C. Gardner, 2013. "Determination of Primary Chemical Constituents of PBX(AF)-108 Warhead Explosive using *microPHAZIR*TM Near Infrared (NIR) Handheld Platform", Annual Conference of the Prognostics and Health Management Society, 2013.
- C. Gardner, and S. Schreyer 2013. "*microPhazir*TM CL-01 Solid Rocket Propellant Quantitative Results". Thermo Fisher Scientific, Tewksbury, MA 01887, USA.
- C. Gardener, and M. Hargreaves, 2012. "Near Infrared Data Report for PBX(AF)-108 Warhead Explosive". Thermo Fisher Scientific, Tewksbury, MA 01887, USA.
- S. Schreyer, 2012, Thermo Scientific Training Course Tutorial Series: "Building Quantitative (PLS-1) Models". Thermo Scientific, Tewksbury, MA 01887, USA.
- S. Schreyer, 2012, "Thermo Scientific Best Practices for Collecting and Evaluating Spectra from *microPhazir*TM NIR handheld platform". Thermo Scientific, Tewksbury, MA 01887, USA.
- L. Biegert, and B. Cragun, 2013, "D-Optimal Design of Experiment for Qualification of *microPhazir*TM Handheld NOR Platform on Experimental Rocket Motor Propellant", Final Report No. TR-034059. ATK Launch Systems, Aerospace Systems, Brigham City, UT 84302, USA.
- G. Bocksteiner, and D.J. Whelan, November 1995, DSTO-TR-0228: "The Effect of Ageing on PBXW-115(Aust.) PBXN-103 and PBXN-105". *Department of Defence, Defence Science and Technology Organization* (DSTO).
- Mattos et al., 2004, "Determination of the HMX and RDX Content in Synthesized Energetic Material by HPLC, FT-MIR, and FT-NIR Spectroscopies", *Química Nova*, Vol. 27, No. 4, pp. 540-544.
- Urbanski et al, 1977, "Handbook of Analysis of measures of Synthetic Polymers and Plastics", John Wiley & Sons, New York, 494 p.
- M. Blanco, and I. Villarroya (2002) NIR spectroscopy: "A rapid-response analytical tool". *Trends in analytical chemistry* 21:240-250.
- H.W. Siesler, Y. Ozaki, S. Kawata, and M. Heise (Eds) (2002). *Near Infrared Spectroscopy Principles, Instruments*, Wiley-VCH.
- microPhazir*TM User Manual, Thermo Scientific Handheld Near-Infrared Analyzer. Thermo Fisher Scientific, Tewksbury, MA 01887, USA.
- Performance Characteristics of the Agilent 1100 Series Modules and Systems for HPLC. Agilent Technologies, Publication Number 5965-1352E.
- A.N. Gent (1958), On the relation between indentation hardness and Young's modulus, *Institution of Rubber Industry – Transactions*, 34, pp. 46–57.
- "Shore (Durometer) Hardness Testing of Plastics". Retrieved 2006-07-22.